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(NASA-CR-105033) DEVELOPMENT OF TECHNIQUE
FOR AR COATING AND NICKEL AND COPPER
METALLIZATION OF SOLAR CELLS: FPS SUBJECT,
PRODUCT DEVELOPMENT Quarterly Technical
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QUARTERLY TECHNICAL REPORT NO. 1

for

DEVELOPMENT OF TECHNIQUE FOR
AR COATING AND NICKEL AND COPPER
METALLIZATION OF SOLAR CELLS

FPS PROJECT

PRODUCT DEVELOPMENT

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A handwritten signature in dark ink, appearing to read 'C. G. Rominger', is written over a horizontal line.

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"The JPL Low-Cost Solar Array Project is sponsored by the U. S. Department of Energy and forms part of the Solar Photovoltaic Conversion Program to initiate a major effort toward the development of low-cost solar arrays. This work was performed for the Jet Propulsion Laboratory, California Institute of Technology by agreement between NASA and DOE."

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PREFACE

The information presented in the report on the "Development of Techniques for AR Coating and Nickel-Copper Metallization of Solar Cells," represents work performed by Photowatt International, Inc. of Tempe, Arizona; Electro-Science Lab (ESL) of Pennsauken, New Jersey; and Vanguard Pacific of Santa Monica, California.

The JPL Technical Manager is Mr. L. Sanchez.

1.0 SUMMARY

Solar cells were fabricated using the Photowatt International, Inc., production process. One hundred 3" cells with 800 Å of silicon nitride over N+/P junction, and evaporated aluminum metal (on the back side) were delivered to ESL for nickel printing. Initially two nickel pastes were defined by ESL as Lot 1051-21A and Lot 1051-21B; each lot had a different type of borosilicate frit. After application of nickel paste these solar cells were sent to Vanguard Pacific for brush copper plating.

Electrical and mechanical data taken from Lot 1051-21A and Lot 1051-21B indicated a need to increase borosilicate frit and silver fluoride (AgF). Three more pastes were formulated by ESL. Paste C is Lot 1051-21A with an increase in Type A frit and AgF, Paste D is Lot 1051-21B with an increase in Type B frit and AgF, and Paste E is a new nickel paste containing a different blend of borosilicate frit.

Electrical, mechanical and visual data were recorded for three groups of nickel pastes using various fire-in temperatures and time cycles.

The visual cell evaluation after brush copper plating revealed copper residue over the surface of most cells. There was an enlarging of grid lines during the copper plating. There was also an area along the edge of copper plating (approximately 1/4") in which the nickel was removed.

Several initial cells were found to have low adhesion levels

when subjected to qualitative (tape test and mechanical scratching) testing.

The nickel paste on some cells disclosed minor blistering after firing, but had good adhesion to tweezer-push and tape tests.

Electrical and mechanical data indicate all nickel paste groups, at all temperatures and times, have ohmic contact.

Quarter cells of each nickel group are being evaluated using techniques such as SEMS, SIMS and Beta-scan.

2.0 TECHNICAL PROGRESS

Studies of AR Coating Thickness and Nickel-Copper Metallization on Flat Plate Solar Cells.

During this report period, one thickness of silicon nitride (800 Å) and several nickel paste groups were investigated in conjunction with a brush copper plating process for the purpose of identifying one or more fabrication sequences which yielded at least 10% efficient N+/P+ flat plate solar cells.

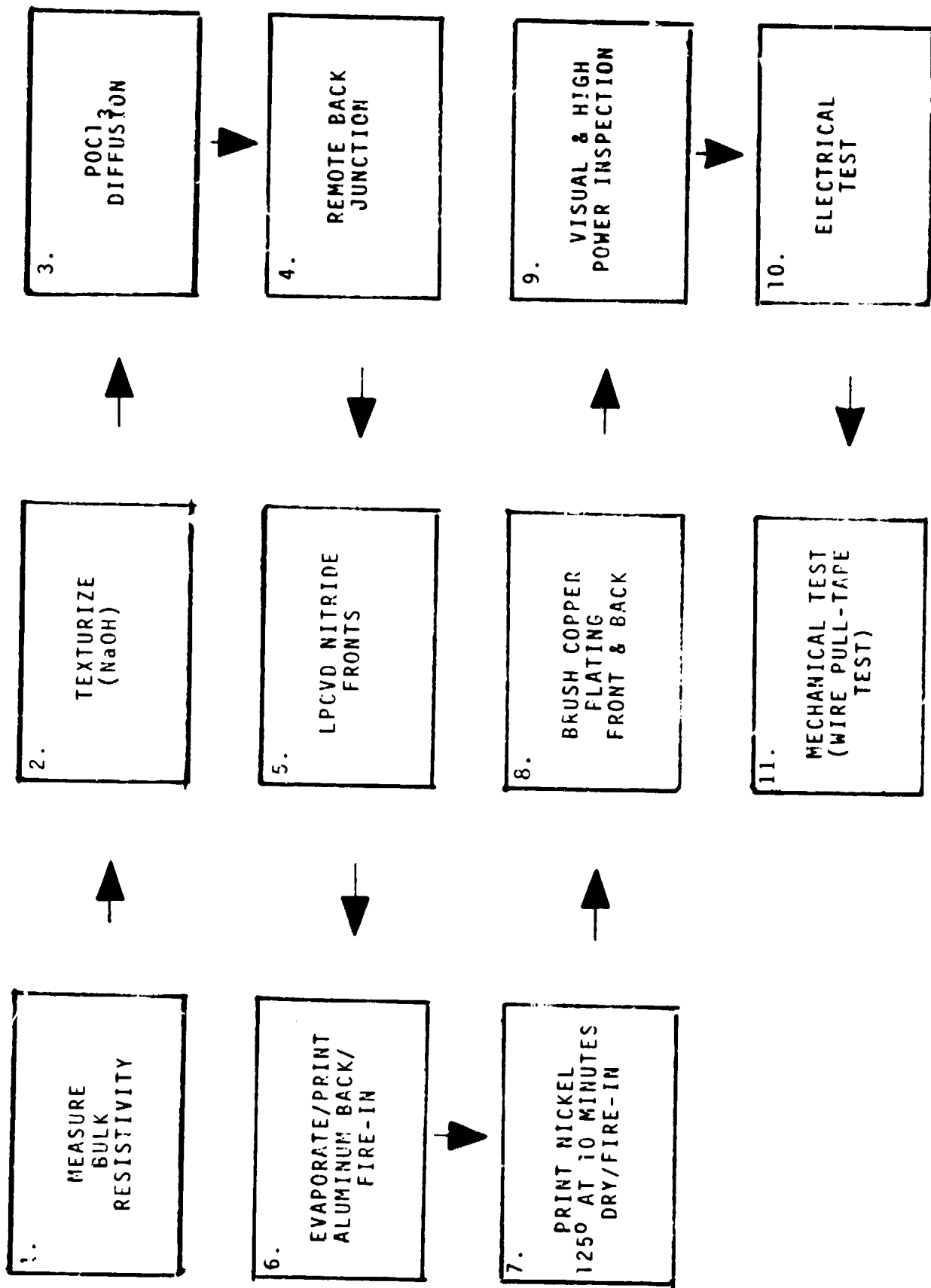
Preliminary experiments began with the selection of two subcontractors, Electro-Science Lab (ESL) or Pennsauken, New Jersey, who is formulating the nickel paste and Vanguard Pacific of Santa Monica, California, who is performing the brush copper plating.

Photowatt International, Inc. processed solar cells as shown in Figure 1; steps 1 through 6 and 9, 10, and 11. Steps 7 and 8 were performed respectively by Electro-Science Lab and Vanguard Pacific.

One-hundred solar cells were delivered to ESL for printed nickel paste application. ESL formulated two nickel pastes (Lot 1051-21A and Lot 1051-21B) which contained different compositions frit and AgF borosilicate. ESL printed nine cells with Lot 1051-21A nickel paste and nine cells with Lot 1051-21B nickel paste. These were returned to Photowatt for evaluation after firing-in.

There were three conditions of firing-in after drying at 125°C for 10 minutes.

FIGURE 1
OUTLINE OF PROCESS SEQUENCE



Firing-in conditions:

625°C peak, 45 minute cycle in a box furnace.

625°C peak, 23 minute cycle in a box furnace.

700°C for 1 minute without preheating in a box furnace.

The purpose for different firing-in cycles with the initial cells was to qualitatively define the following parameters:

- o Adhesion of nickel to silicon.
- o Penetration of nickel through 800 Å of Si_3N_4 .
- o Provide nickel metallization for brush copper plating.
- o Determination of ohmic contact and series resistance ranges.

Nine samples of Lot 1051-21A and Lot 1051-21B nickel printed cells were submitted to Vanguard Pacific for brush copper plating. A summary of the brush copper plating technique is provided in Appendix A.

During the course of activities several cells were broken and used in characterization of Ni pastes and brush copper plating.

The I-V characteristics of these initial 3" cells, printed with Lot 1051-21A nickel paste, are reported in Table 1.

The I-V characteristics of the initial cells printed with Lot 1051-21B nickel paste are reported in Table 2.

The resulting I-V characteristics were discussed with ESL, and resulted in ESL increasing the borosilicate and AgF to improve the physical contact strength and electrical parameters.

Three new pastes were formulated by ESL:

- o Paste C- Lot 1051-21A with an increase

TABLE 1
ELECTRICAL TEST RESULTS
OF 3" CELLS USING LOT 1051-21A PASTE

| CELL NUMBER | Isc (mA/cm ²) | Voc (VOLTS) | F I R E C Y C L E | | |
|----------------|---------------------------|-------------|-------------------|----------|---------------|
| | | | FURNACE TYPE | TEMP (C) | TIME (MIN) |
| 1 | 22 | 0.523 | IR Belt | 625 | 5 |
| 2 | 23 | 0.552 | IR Belt | 625 | 5 |
| 3 | 13 | 0.427 | IR Belt | 625 | 10 |
| 4 | 25 | 0.522 | Box | 700 | 10 |
| 5 | -0- | 0.551 | Box | 700 | 1 |
| 6 | 4.2 | 0.545 | Box | 700 | 1 |

in borosilicate and AgF.

- Paste D- Lot 1051-21B with an increase in borosilicate and AgF.
- Paste E- New composition of borosilicate frit.

Experimental cells were again processed by Photowatt, utilizing steps 1 to 6 (see Figure 1), and sent to ESL for printed nickel metallization.

ESL printed six cells each with pastes C, D and E. Each group of cells was fired at different temperatures and time durations, after a 125⁰C drying cycle of 10 minutes.

The groups were sent to Vanguard Pacific for brush copper plating. There was an unexpected loss of cells due to breakage at Vanguard; as a result only one fire-in temperature could be evaluated. Electrical results are in Table 3. Additionally all samples exhibited very low peel pull strengths after copper plating.

Photowatt requested that ESL send samples of the three nickel pastes for better control on the process and to increase the quantity of cells being processed. Photowatt utilized the three samples of nickel paste to process cells up to brush copper plating.

After initial cell processing and printing, all pastes were dried at 125⁰C for 10 minutes. Three firing cycles were defined as follows:

- | | |
|----------------------|--|
| o 625 ⁰ C | 2 minute heat-up, 10 minute soak for a total of 12 minutes. |
| o 650 ⁰ C | 2 minute heat-up, 10 minute soak for a total of 12 minutes. |
| o 700 ⁰ C | 2 minute heat-up, 5 minute soak for a total of 7 minutes. |

TABLE 2
ELECTRICAL TEST RESULTS
OF 3" CELLS USING LOT 1051-218 PASTE

| CELL NUMBER | Isc(mA/cm ²) | Voc(VOLTS) | F I R E C Y C L E | | |
|----------------|--------------------------|------------|-------------------|---------|---------------|
| | | | FURNACE TYPE | TEMP(C) | TIME (MIN) |
| 1 | 20 | 0.448 | IR Belt | 625 | 5 |
| 2 | 25 | 0.564 | IR Belt | 625 | 5 |
| 3 | -0- | 0.544 | IR Belt | 625 | 5 |
| 4 | 20 | 0.505 | IR Belt | 625 | 10 |
| 5 | 21 | 0.555 | IR Belt | 625 | 10 |
| 6 | 11 | 0.183 | Box | 700 | 1 |
| 7 | 24 | 0.572 | Box | 700 | 1 |

TABLE 3
ELECTRICAL TEST RESULTS
OF 1½" CELLS

| CELL #/ Ni PASTE TYPE | Isc (mA/cm ²) | Voc (VOLTS) | F I R E C Y C L E | | |
|-----------------------------|---------------------------|-------------|---------------------|----------|---------------|
| | | | FURNACE TYPE | TEMP (C) | TIME (MIN) |
| 1-C | 29.9 | .520 | Box | 650 | 10 |
| 2-D | 28.0 | .540 | Box | 650 | 10 |
| 3-E | 27.5 | .540 | Box | 650 | 10 |

All samples were given a tape test after firing, all samples indicated no lifting of nickel from Si_3N_4 . (Note: These nickel pastes will not wet solder after fire, thus pull tests were not performed until after copper plating).

Samples were provided to Vanguard Pacific with the above variations of nickel pastes and firing cycles.

Brush copper plating was used to deposit copper on the front nickel and aluminum backs by Vanguard Pacific. Cells from the different Ni paste groups were returned to Photowatt for evaluation.

Pull test results of samples returned from Vanguard Pacific are presented in Table 4. The pull test values reported in Table 4 represent both the (90°) peel strength and shear strength of the metal layers when a flat ribbon (.002 x .062) was attached to the plated copper. A mildly activated flux was utilized to solder the ribbon to the cells.

Electrical test results of the samples returned from Vanguard Pacific are presented in Table 5. From the electrical test results, fill factor, I_{sc} (per cm^2) and efficiency were calculated and are also reported in Table 5.

Mechanical scratching and tape tests were applied to samples returned from Vanguard Pacific and results presented in Table 6. A visual and high power microscope inspection were performed on the returned samples and reported in Table 6.

TABLE 4
MECHANICAL TEST RESULTS

| CELL #/ Ni PASTE TYPE | FIRE CYCLE | | Ni PASTE/Cu PLATE | | Al PASTE/ Cu PLATE BACK SHEAR PULL STRENGTH (GRAMS) |
|-----------------------------|------------|------------|---|---------------------------------|---|
| | TEMP(C) | TIME(MINS) | FRONT SHEAR PULL STRENGTH (GRAMS) | 90° FEEL STRENGTH (GRAMS) | |
| 1-C | 625 | 10 | 980 | 100 | 900 |
| 2-C | 650 | 10 | 330 | 25 | 900 |
| 3-C | 700 | 5 | 170 | 17 | 900 |
| 1-D | 625 | 10 | 290 | 25 | 900 |
| 2-D | 650 | 10 | 190 | 20 | 900 |
| 3-D | 700 | 5 | 260 | 24 | 900 |
| 1-E | 625 | 10 | 685 | 75 | 800 |
| 2-E | 650 | 10 | 1000 | 120 | 900 |
| 3-E | 700 | 5 | 600 | 65 | 900 |

TABLE 5
ELECTRICAL TEST RESULTS

| Ni PASTE CELL # | FIRE TEMP (C) | FIRE TIME (MIN) | I _{sc} (mA/cm ²) | V _{oc} (VOLTS) | F.F. | EFF (%) |
|-----------------------|------------------|--------------------|---------------------------------------|-------------------------|------|---------|
| 1-C | 625 | 10 | 23 | 0.55 | 0.31 | 3.64 |
| 2-C | 650 | 10 | 25 | 0.56 | 0.39 | 4.90 |
| 3-C | 700 | 5 | 25 | 0.54 | 0.40 | 5.35 |
| 1-D | 625 | 10 | 18 | 0.45 | 0.26 | 2.14 |
| 2-D | 650 | 10 | 25 | 0.57 | 0.62 | 8.78 |
| 3-D | 700 | 5 | 25 | 0.58 | 0.63 | 9.27 |
| 1-E | 625 | 10 | 24 | 0.56 | 0.36 | 2.39 |
| 2-E | 650 | 10 | 25 | 0.56 | 0.48 | 6.40 |
| 3-E | 700 | 5 | 24 | 0.57 | 0.65 | 8.99 |

TABLE 6
VISUAL & HIGH POWER EVALUATION
RESULTS

| Ni PASTE & CELL# | FIRE CYCLE | | QUALITATIVE ADHESIVE TESTS | | VISUAL & POWER INSPECTION | |
|---------------------|------------|-----------|-------------------------------|--------|------------------------------|---------------|
| | TEMP(C) | TIME(MIN) | BUSS | FINGER | Cu RESIDUE | Ni RESIDUE |
| 1-C | 625 | 10 | OK | ML | YES | YES |
| 2-C | 650 | 10 | OK | ML | YES | YES |
| 3-C | 700 | 5 | ML | OK | YES | B |
| 1-D | 625 | 10 | OK | ML | YES | NO |
| 2-D | 650 | 10 | OK | L | YES | ETC |
| 3-D | 700 | 5 | ML | L | YES | NO |
| 1-E | 625 | 10 | OK | OK | YES | B |
| 2-E | 650 | 10 | OK | ML | YES | YES |
| 3-E | 700 | 5 | OK | ML | YES | YES |

Note 1: Codes and abbreviations for above columns: OK (test results successful); YES (Cu residue and/or Ni residue); NO (no visible Cu residue and/or Ni residue); ETC (nickel exposed through copper); B (Ni blistered); ML (minor lifting); L (lifting).

Note 2: All cells evaluated revealed removal of nickel along the edge of the copper plating.

Note 3: Copper lifting was only on some fingers or buss bars not the entire grid pattern, as determined by tape test and tweezers.

Note 4: All cells evaluated had some metal--aluminum or copper around the isolation edge, and copper residue over the surface.

3.0 SUMMARY OF DATA

The salient points of this quarterly report on ESL nickel pastes and Vanguard Pacific brush copper plating are as follows.

The ESL nickel paste Lot 1051-21A exhibits better electrical characteristics at low temperature fire-ins as indicated from test results. (Table 1, cell number 4 with $I_{sc} = 25.0 \text{ mA/cm}^2$ and $V_{oc} = 522 \text{ mV}$).

The ESL nickel paste Lot 1051-21B exhibits better electrical characteristics at high temperature fire-ins as indicated from test results. (Table 2, cell number 7 with $I_{sc} = 24.0 \text{ mA/cm}^2$ and $V_{oc} = 572 \text{ mV}$).

There was evidence of ohmic contact from both pastes, as indicated in Table 1 and 2, with appreciable V_{oc} .

The test results in Table 1 and 2 lead to ESL formulation of nickel pastes C, D, and E.

ESL nickel paste group C, D and E, mechanical test results (Table 4), electrical test results (Table 5) and visual/high power evaluations (Table 6) are summarized as follows.

There is evidence with paste C of:

- Good adhesion of nickel to silicon and high mechanical shear pull strength at low fire-in temperatures.
- Ohmic contact as indicated by appreciable V_{oc} at all fire-in temperatures.
- Poor I-V characteristics, as indicated in Table 5, at all fire-in temperatures.
- Acceptable shear strengths at low 625° fire-in temperatures.

- Low 90° peel strengths at all fire-in temperatures.

There is evidence in Paste D of:

- Poor adhesion of nickel to silicon nitride.
- Good ohmic contact.
- Fair I-V characteristics, as indicated in Table 5, at 650° and 700° fire-in temperatures.
- Low 90° peel strengths at all fire-in temperatures.
- Low shear strengths at all fire-in temperatures.

There is evidence in Paste E of:

- Good adhesion of nickel to silicon nitride, high shear pull strength at all fire-in temperatures.
- Good ohmic contact, as indicated by appreciable Voc at all temperatures.
- Fair I-V characteristics, as indicated in Table 5, at 700°C fire-in temperatures.
- Moderate to good shear and 90° peel strength as compared to the requirements of the contract.

4.0 TENTATIVE CONCLUSIONS

Experimental results have led to the following tentative conclusions and recommendations.

The adhesion of all ESL nickel pastes, (tested to date) is reduced significantly when subjected to "Selectron" acidic and alkaline brush copper plating solutions. This is presently thought to be the result of a combination of thermally induced stress (not electrode) and chemical attack of the frit. Chemical attack of the frit occurs principally at the interface with the silicon solar cell.

As all groups of ESL nickel pastes are presently formulated, the AgF is penetrating the 800 Å of Si_3N_4 and ohmic contact is occurring at all fire-in temperatures.

During the brush plating process, fingers and buss bars tend to spread considerably.

It appears, from the results to date, that a 10% efficient cell can be produced.

5.0 PLANS

- Evaluate samples of printed nickel and brush copper plating.
 - A. Soak nickel printed cells @ 90°C in neutral alkaline copper solution.
 - B. Do thermal shock test on nickel printed cells (590°C temperature and LN₂).
 - C. Do thermal expansion coefficient measurement on nickel printed cells.
- Start reliability testing of the contact systems.
- Improve adhesion and open-circuit voltage.
- Minimize the impact of copper plating on adhesion of nickel paste to the silicon nitride.
- Investigate the rheology of the nickel paste.
- Reduce series resistance.

APPENDIX A

The theory of brush plating is similar to bath plating but the procedure resembles arc welding. As can be seen from Figure A-1, one lead of the plating rectifier is connected to the part to be plated, which acts as a cathode. The other lead fits into the work tool, called a "stylus", which is an anode of the proper size and shape to contact a good part of the area to be built up. The anode is wrapped with a swab and the solution is pumped onto the swab. With the current on, the anode swab is brushed over the area to be plated until the desired thickness of deposit has been achieved. Rates of deposition with this technique are extremely high. The resulting deposits are hard, low in porosity, very pure, easily solderable and of high conductivity. Porosity is 75% less than that obtained in a bath deposit of identical thickness. Prior to brush plating, which is normally activated by reverse etching, this is easily achieved by simply reversing the process direction with a substitution of etching or activating solution. The average rate of deposition of copper is about 1-2 mils/minute with current densities ranging from 2000-6000 Amp/hours per square foot. This is at least 100 times faster than normal electroplating techniques.

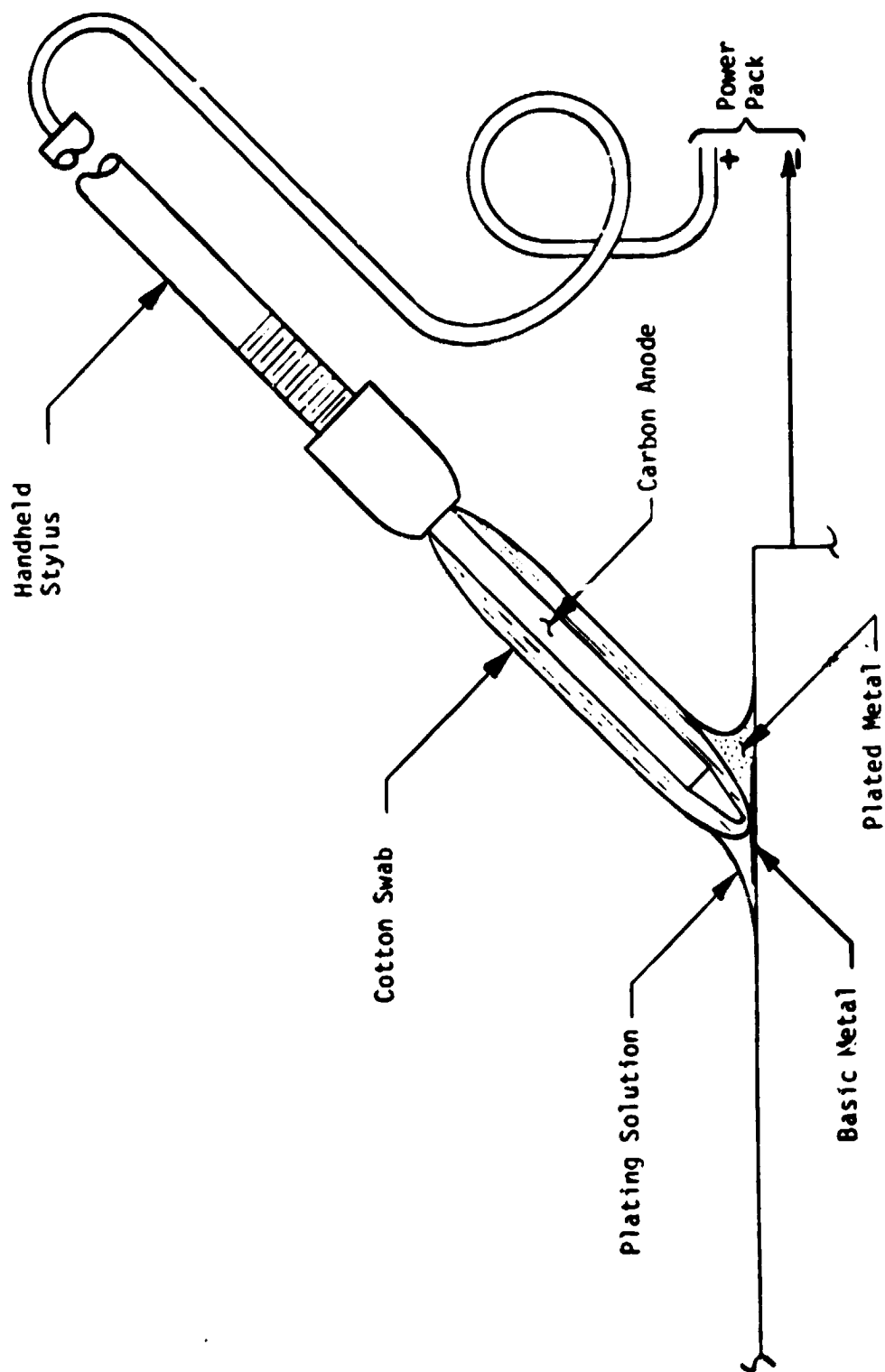


Figure 1-A. Schematic of Brush or Selective Plating Operation